

MANUFACTURE OF SALICYLIC ACID

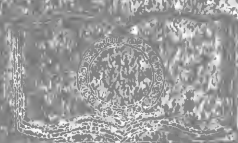
BY

S. W. KENDALL

ARMOUR INSTITUTE OF TECHNOLOGY

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The manufacture of salicylic
acid

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THE MANUFACTURE OF SALICYLIC ACID

A THESIS

PRESENTED BY

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TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

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The Manufacture of Salicylic Acid.

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THE MANUFACTURE OF SALICYLIC ACID

Introduction.

During the early months of 1913 when the price of synthetic organic chemicals was steadily mounting to heights previously undreamed of, a number of Illinois druggists and jobbers formed an association for the purpose of manufacturing for their own use those compounds whose scarcity was most severely felt. Among the organic compounds in this list were salicylic acid, sodium salicylate and salol. The firms manufacturing chemical apparatus were called upon but in every case demanded such exorbitant fees or such long periods of time that it was decided to go ahead and with the aid of the literature and, such small-scale experimentation necessary, to develop the desired apparatus and method of operation.

This work was started in March and the first hundred pounds of pure salicylic acid made by the end of June. It may be stated here that the literature on the subject is old and very indefinite as most of it is found in the German patents. The most recent reference is the "Manufacture of Salicylic Acid" by Sapper in the *Chemist and Druggist* 85,313 ('14) which however is not available as "Chemical Abstracts" owns the only copy in the United States. Another reference, "The Salicylates" by Hanzlik in the 1914 Annual Report of the American Medical Association gives a comprehensive review of the literature from the pharmacological and physiological point of view but gives no information of value on manufacture.

Historical.

Salicylic acid was first prepared in 1838 by R. Pira (Annalen 30,151) (A.93,262;1855) by the action of lime on natural salicylic aldehyde. In 1843 Canours (A. 48,61) recognized the methyl ester in oil of wintergreen and prepared the free acid by digesting the oil (Gaultheria procumbens) with milk of lime. This was carried out on a commercial scale until 1874. Gerland in 1852 obtained the acid by the action of nitric acid on anthranilic acid (Chem. Soc. Quarterly 5,133) (J. 1852,493).

Prof. H. Kolbe (A. 86,148;1853) recognized the compound to be a hydroxy acid in that it was readily decomposed into CO_2 and phenol. His famous synthesis of salicylic acid followed in 1859 (A. 113,125; 115,201). This consisted in bubbling carbon dioxide thru phenol containing strips of metallic sodium. This method was later modified (J.pr.Ch. 2 10,89;1874) and finally put into technical form (DRP,426,1377). The Kolbe process, which will be fully described later, was greatly improved in 1884 by Schmitt (DRP 29939). This Schmitt modification is the basis of the process now used since 1885.

The Kolbe Process.

The following account of the Kolbe process as it was carried on at the Chemischen Fabrik Homburg vor der Höhe was taken from "Weitere Mitteilungen zur Streitfrage über das Kolbesche Salicylsäurepatent" 1876 A. Seidel, Polytech. Buchhandlung:

IN a large iron kettle phenol is heated with the theoretical amount of caustic soda at a temperature of 183°C. until no more water distills. Then dry carbon dioxide is admitted and the temperature raised to 200° or over. In order to reach this high temperature a direct-fired or oil bath autoclave (Fig. 1) is used. This is made of cast iron and has an inside diameter of 1500mm. and height of 700mm. The autoclave has a stirring mechanism and bottom plow to prevent burning the fusion. Stationary arms are also employed inside to help break up lumps. The bottom and sides of the autoclave are made quite thick so as to avoid their being burned thru. Coke or producer gas are the fuels used.

Two condensers are used, the first collecting the larger portion of the phenol which distills over. Both are placed in larger vessels connected to water and steam supply, by means of which the temperature of the phenol may be regulated. It is of particular importance that the phenol be kept in the liquid state as several disastrous explosions are recorded due, no doubt, to the stopping up of the outlet by crystallized phenol. This process gave a very impure product, of bad color and almost impossible to purify, and hence has been entirely abandoned.

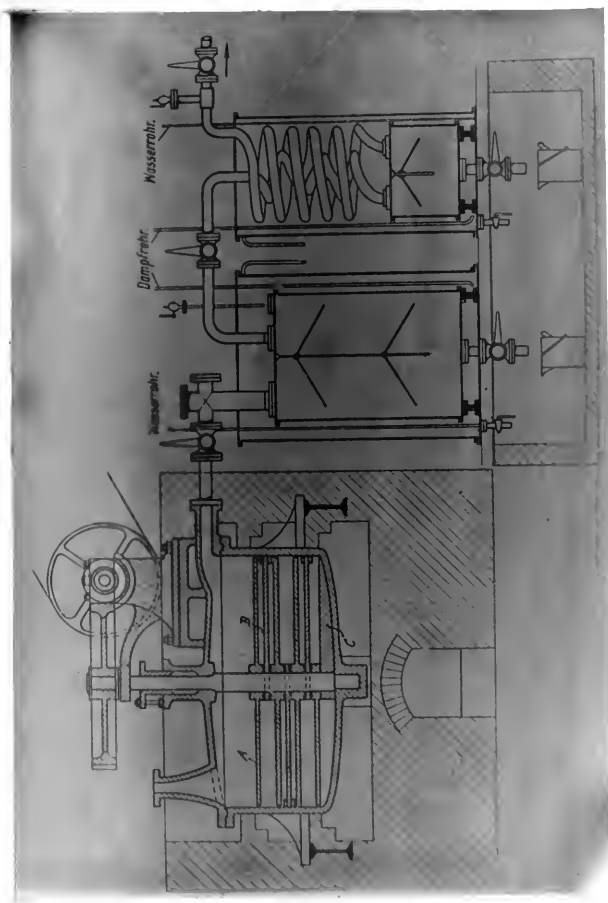


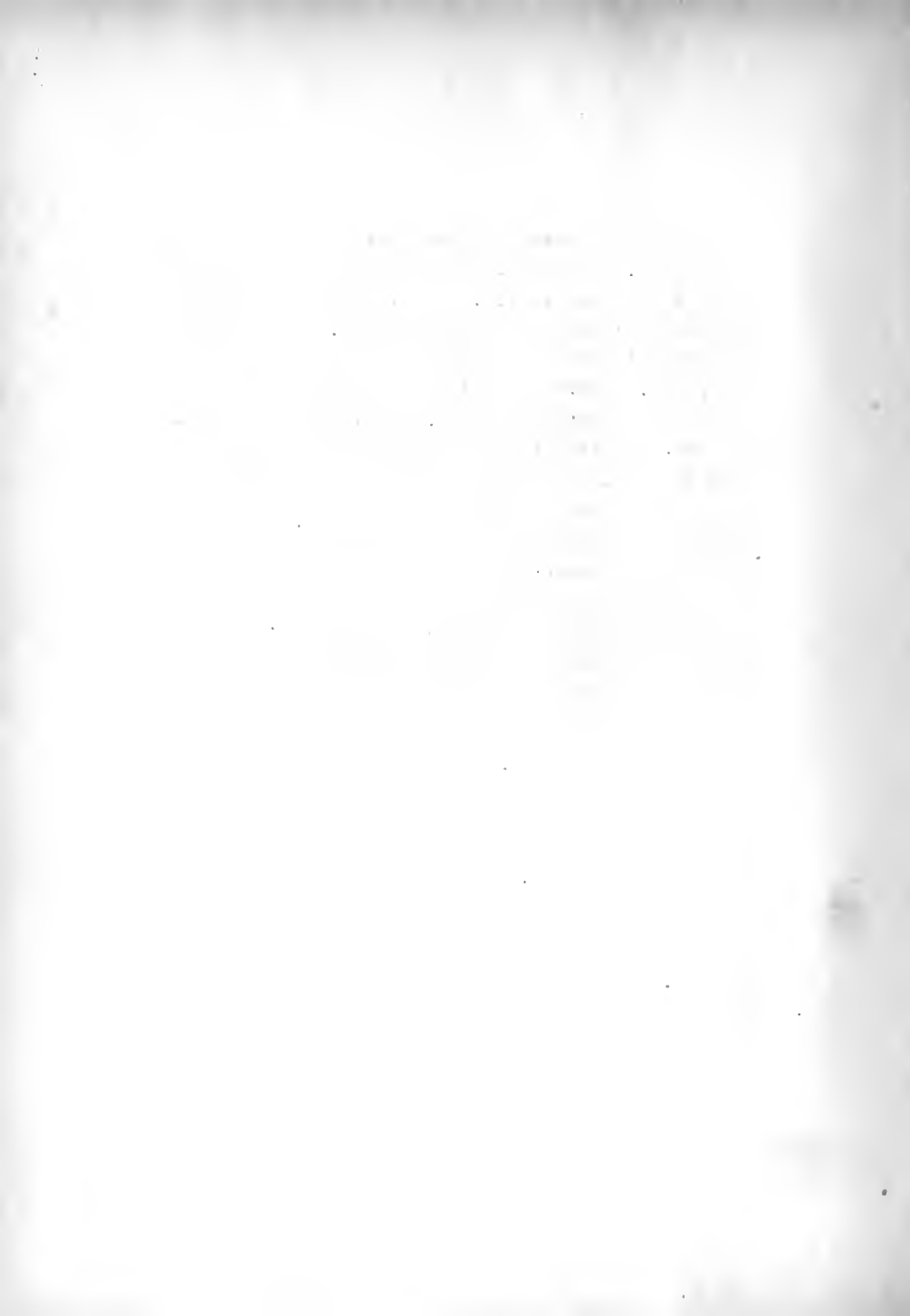
Fig. 1.



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This autoclave has a capacity of 300 kg phenol per charge, using 127.84 kg sodium hydroxide and 70.18 kg carbon dioxide. The theoretical yield of disodiumsalicylate from this is 290.43 kg or 220 kg of free salicylic acid and 150 kg of phenol. The yield, however, of free acid never exceeded 90% of the theory due to decomposition from overheating. In addition the recovery of phenol was less than 150 kg because it had to be purified before being used again, this necessitating certain losses. The salicylic acid itself always retained considerable quantities of phenol which was very difficult or even impossible to eliminate.

The commercial salicylic acid of this period was notorious for the impurities which it contained totaling in many instances 11%.



The Schmitt Patents.

The Schmitt patents, as has been previously mentioned, are the basis of the process now used for large scale manufacture of salicylic acid.

The 1884 patent reads as follows

The dry phenolates or phenolate are or is rapidly dried and placed in an autoclave and dry carbonic acid is introduced under pressure as long as necessary. The vessel is well cooled during the pumping otherwise basic salicylate is readily formed with separation of phenol.

The vessel is kept closed as long as the carbonic acid is not perfectly absorbed and any excess of pressure present. The mass is then allowed to stand for some time. The vessel is then heated in an air bath to 120-140°C. to convert to normal sodium salicylate.

OR. The closed autoclave is connected by a tube and valve to a cylinder containing liquid carbon dioxide. Under the high pressure the salt rapidly saturates. When complete heat is applied to the closed vessel.

OR. The required weight of solid carbonic acid is thrown in and the vessel quickly closed and heated as before.

The 1886 patent discovers that cooling and standing are not necessary. Carbon dioxide under pressure is introduced into the material in the autoclave maintained at 120-140°C. The temperature must not rise above this or phenol separates. The proper pressure must also be used.

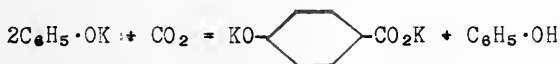
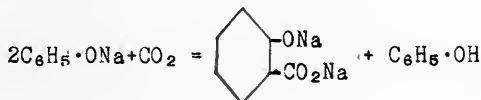


This is the most definite information which could be found in the literature. It provides a working basis but leaves for investigation the time required, the proper pressure to use, the type of autoclave and the general technique to employ.

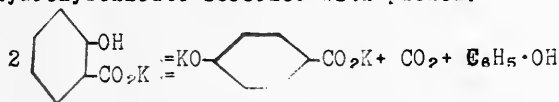
Chemistry.

Salicylic acid is the ortho-hydroxy benzoic acid; The meta- and para- bodies are both made but neither has any industrial application.

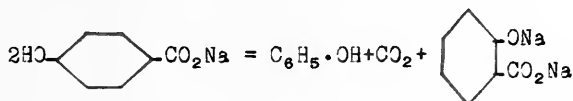
The old Kolbe process heats phenol with dry sodium or potassium hydroxide obtaining sodium and potassium phenolate respectively. When heated at 183-200° with dry carbon dioxide the first yields sodium salicylate and phenol, but the potassium phenolate gives p-hydroxybenzoate of potassium:



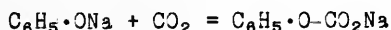
In both cases only one half of the phenol is used up. The reaction between sodium phenate and carbon dioxide begins under 100°, progresses most rapidly between 170-180° and remains unchanged to 300°. Between 100-150° potassium phenate likewise forms dipotassium salicylate but above this temperature the isomeric p-hydroxybody appears and at 220° is the sole product. By holding the primary potassium salicylate at 220°, dipotassium-p-hydroxybenzoate is formed with phenol:



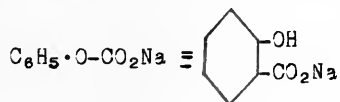
With the same treatment primary sodium salicylate gives not a trace of the para body but is simply changed into disodiumsalicylate with loss of phenol and carbon dioxide. If, however, primary p-hydroxybenzoate of sodium is heated to 280-290° in carbon dioxide it is converted into disodium-salicylate:



The Schmitt process, unlike the preceeding, yields sodium phenylcarbonate from sodium phenate and carbon dioxide at ordinary temperatures:

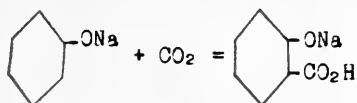


If this salt is maintained a sufficient time at about 140° out of contact with air, it rearranges giving the same weight of sodium salicylate:



This old theory of the formation of sodium salicylate has been opposed by S. Tijnstra Bz in a series of papers (B. 38, 1375/1905; 39, 14 /1906/; 45, 2827 /1912/). His theory, which is well founded, is that the end product is sodiumphenate-o-carbonic acid which rearranges. This is borne out by the

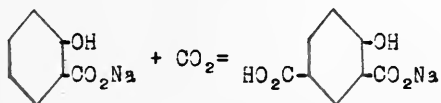
fact that sodium phenate adds carbon dioxide directly:



This subject is thoroughly discussed by Brunner:
 "Über den chemischen Prozess der Synthesen durch die
 Aufnahme der Kohlensäure" (A. 351, 313 /1907/).

The crude sodium salicylate may contain three impurities: the para body, hydroxy isophthalic acid, and cresolic (hydroxy toluic) acids. The formation of the first of these has already been discussed, i.e. its presence is due to potassium hydroxide in the sodium hydroxide used. It has also been stated by Hoffman that the para salt is formed in small quantities if the temperature at which the carbon dioxide is admitted is too low.

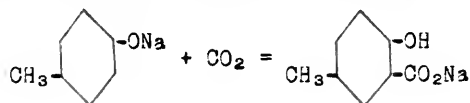
Hydroxy isophthalic acid is formed, sometimes to the extent of 2%, if the temperature is allowed to rise above 145°C. This due to the action of the gas on the sodium salicylate already formed:



The most objectionable contamination from the physiological point of view is the cresolic acid or acids. These are the o-, m-, and p- hydroxy toluic bodies, the nearest homologues to the hydroxy benzoic acids. They are formed by the Schmitt reaction in



exactly the same way, their source being the cresols in the phenol used. As p-cresol is the predominating impurity in a poor phenol, it follows that the para hydroxy toluic acid will be formed:



Autoclaves.

The first and most important problem for solution was the design of autoclave to use. The preliminary experiments were carried out using a small laboratory autoclave. Sodium phenate was made by heating to dryness in an open iron pot, molecular proportions of C.P. phenol and sodium hydroxide with enough water to dissolve the hydroxide. This material was well stirred during the drying operation and was used in pieces four mesh and under. Fifty gram portions were used for each experiment.

The sample of sodium phenate was placed in the autoclave which was then closed. The heat was applied and carbon dioxide admitted from a cylinder. The pressure of the gas was changed by five pounds per sq.in. for each run, the maximum pressure used being 200# per sq.in. The rate of absorption of the gas as indicated by the pressure gauge was observed in each case as well as the rate of temperature rise and the ease of controlling that rise so as not to exceed 145°. The result of these 40 experiments follows:

1. The rate of absorption of carbon dioxide increased directly as the pressure up to 90# per sq.in.
2. The rate of increase above 90# pressure became rapidly less.
3. Between 145# and 200# per sq.in. the rate of absorption was constant.
4. The temperature regulation up to 35# was easy, the heating flame not being touched until a temperature of 140° was reached when it was lowered slightly.

5. At all pressures above 95# the temperature tended to change by jumps, constant manipulation of the heating flame being required and in several instances (above 140#) cold water thrown over the autoclave necessary.

6. The product obtained in each case up to 95# could not be distinguished from the next, all being of a uniform light brown color and yielding almost identical amounts of free acid and tarry matter on precipitation.

7. Above 95# the crude salt rapidly colored, changing from darker browns to purplish-red in the worst cases. These colored salts yielded more and more tar and less free acid as the color became more vivid.

8. The more the color, the larger the percentage of free phenol and hydroxy iso-phthalic acid found.

From this data it is seen that the largest yield of highest purity, obtainable with easy regulation was at 90# per sq. in. which pressure was also at the point of optimum absorption rate.

Having determined the working pressure (90#) and hence the thickness of wall required for the autoclave, the next consideration was the design and size. The first autoclave used was a steam-jacketed cylinder 2 ft. in diameter and 2 ft. 10 in. deep. This was filled about two thirds full (20#) with screened dry sodium phenate, carbon dioxide admitted at 90# pressure and heated at 140°C. until absorption of gas seemed complete. When cool the crude salt, which had packed down quite

hard, was removed in three inch layers at a time, each layer being thoroughly mixed and sampled. Fifty gram samples from each layer were dissolved in water and the free salicylic acid precipitated, dried and weighed. The upper nine inches seemed to have been almost completely converted but the layers below this rapidly decreased in acid content the lower twelve inches containing less than one percent salicylic acid. This may be explained by the fact that the treatment had gradually broken up the lumps into powder which finally packed down so hard that no gas could penetrate.

Next, an attempt was made to assure the gas getting to the bottom by putting in a perforated false bottom whose under space had constant communication with the upper gas thru a pipe. A similar run was made using this arrangement, sampling as before. The result was very much the same; the upper nine inches was completely converted and also the lower three inches but the intermediate region was quite low. The lower gas layer evidently had been prevented from working by the rapid breaking-up and packing action which quickly closed the channels between the small lumps.

As it was desirable to use if possible this autoclave, of which there were several on hand being used for another purpose, it was decided to add a stirring device which should keep the salt in motion, and thus prevent its packing down. Carrying out this idea, a new cover was made carrying a stirring mechanism as shown in Fig. 2, the thermometer well



Fig. 2.

being shifted to come between the two vertical slats and deep enough to just clear the upper horizontal one. The sodium phenate as before was put in thru the hand hole until the stirrer slats were just covered. The run was made until no more gas seemed to be absorbed and the salt removed in three layers (smaller portions were too difficult to get out on account of the slats). The upper layer was well converted, the middle layer to the extent of 89%, and the lower layer which was well powdered by the stirring action, to the extent of 18%. In another trial it was found impossible to raise this percentage in the lower layer more than 1% by doubling the gassing time. From this it was seen that the deep type autoclave could not be used efficiently as the unconverted sodium phenate could neither be recovered nor separated from the crude sodium salicylate and would in addition liberate free phenol when treated to free the acid.

Another type of autoclave was available, a small horizontal type used for dimethylaniline, fitted with stirrer and steam jacketed 3/4 up each side. The question of temperature regulation was the chief difficulty here seen. The dimensions of this apparatus were 5ft. diameter by 16ft. long. As the quantity of sodium phenate required to fill this was too large to risk, a regulation test was made using 2000 pounds of granulated sodium hydroxide as a charge. One thermometer (steel tube) was placed so that its bulb nearly touched the center stirrer shaft bearing (see Fig. 3); another was put



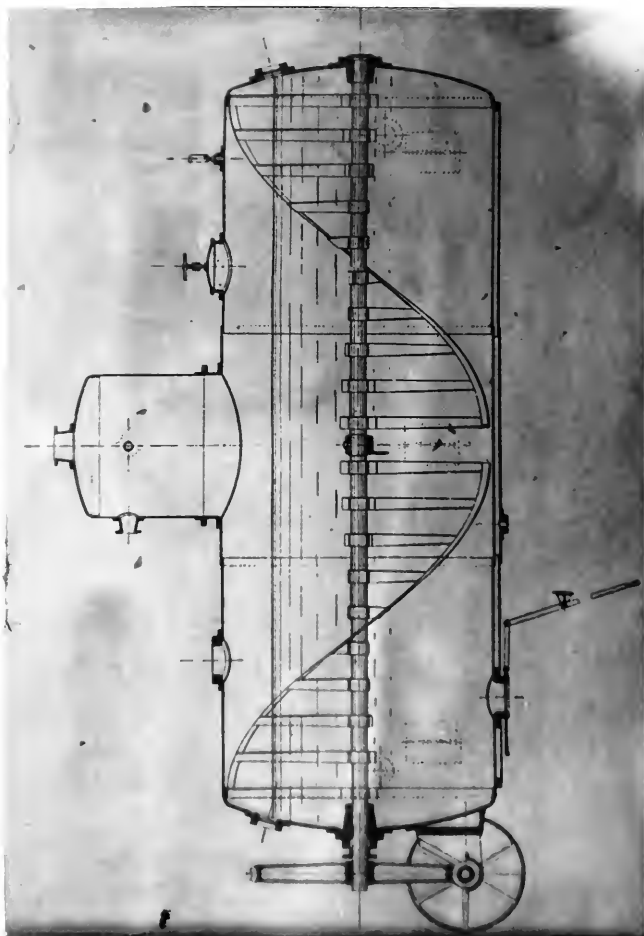


Fig. 3.

directly underneath just thru the inner shell, another directly above, its bulb being in the gas-space and the last about two inches from the right end bearing. The lump sodium hydroxide filled the autoclave to about two inches above the stirrer shaft. The steam was admitted to the jacket and maintained at a pressure of 101 lbs. corresponding to a temperature of 170°C . until the bottom thermometer registered 135° when the pressure was lowered and kept at 16 lbs. (140°). The stirrer was in operation during this time. The bottom thermometer read constantly 140° within 1° ; The thermometer at the center bearing read 132° and the one at the end varied between 130° and 139° . The temperature of the gas-space never exceeded 131° . This showed that it would be impossible to get the regulation desired if the charge used were as large as the size of the autoclave seemed to justify. It was thought, however, that if at any time such large quantities were desired an apparatus of this type with possibly half the diameter and completely jacketed would probably the purpose admirably answer.

From the preceeding experiments it was decided that the best type of autoclave to handle 500# charges was the mechanically stirred with vertical shaft but with greater diameter than height. Carrying out this idea, the autoclave shown in Fig. 4 was designed and built. This has a diameter of 5ft. and height (lower half) of 2ft. 4in. The specification of material for the body



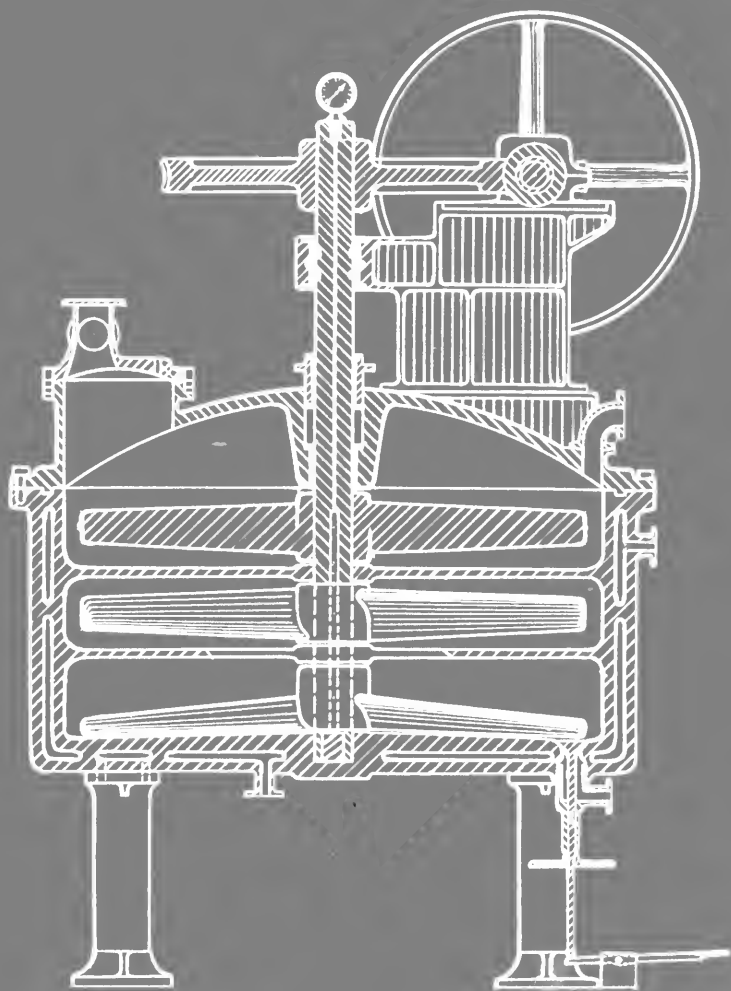


Fig. 4



and stirrer arms which follows was determined by boiling small test pieces of "alkali resistant" irons, furnished by various manufacturers, in sodium phenate solution until the salt was dry and then weighing the test piece to determine the loss in weight:

Material to be a natural semi-white iron not quenched. Composition :

Graphite carbon-----	C.05-%
Combined carbon-----	1.9 to 2.1%
Silicon-----	0.8 to 1.0%
Phosphorus-----	0.20-%
Sulphur-----	0.04-%
Manganese-----	0.30-%

Test pieces within the above composition after the third treatment showed practically no loss in weight on 20 gm. samples.

The apparatus was made quite rigid by casting small connecting braces between the jacket and inside shell. Stirrer blades of curved cross section as shown were used to help turn over the material when dry. The stationary cross arms (another pair are placed at right angles to those shown) were added to catch and break up large lumps which form while the salt is wet. Drive is thru a belt and pulley to a worm and wheel, rotating to the right; the speed reduction is 20 to 1. A thermometer is incorporated in the shaft itself: a quarter inch hole was drilled nearly thru the shaft, the last two inches being 1/16". The lower 2ft.4in. was

drilled to 1" diameter and the last three inches reamed out to 2 1/2" diameter. A plug was made for this last, 0.003" over size so that the shaft itself would have to be heated before the plug could be driven in. An Arnold air gauge reading to two ounces per sq.in. was tapped into the upper end of the shaft, and made air tight by use of white lead in oil. Inverting the shaft, mercury was poured into the well up to the 2 1/2" portion; the end of the shaft was then heated, the inside of the hole wiped with flake shellac which melted and the plug driven in under a press. When turned right end up the confined air filled the gauge and part of the 1/4" bore so that when the mercury was heated, its expansion would force the air into the gauge causing it to register. Calibration of the gauge to read degrees Centigrade, instead of ounces, was done as follows:

The autoclave was nearly filled with water, which was kept just boiling by admitting steam to the jacket. The stirrer was operated during this time. After the water had been boiling for some time and a steady stream of steam escaping from the open carbon dioxide pipe (to right in Fig. 4), the position of the gauge pointer on the scale was marked as 100°. The 140° point was obtained in a like manner using commercial xylol. The boiling point of the first fifty percent of the liquid was between 140.4° and 139.2° which gave a reading close enough to be used. The distilled vapor here was caught in a condenser.

To determine 160° live steam was used. This temperature corresponds to a dry steam pressure of 75# per sq.in. The jacket therefore maintained at this pressure for some time and then steam after passing a separator admitted to the inside of the autoclave at the same pressure. The gauge reading obtained here was called 160°. It may be noted here that after three months constant service, this thermometer was again calibrated by water and steam and found to read correctly.

The three-way connection on the cover of the autoclave is connected to valves by means of which water, steam, and sodium phenate solution (middle) respectively may be admitted. Carbon dioxide enters thru the pipe shown at the right, passing a safety and reducing valve. A ground discharge valve of the poppet type is used, opened by a foot pedal and locked shut by a hand wheel.

The upper jacket connection has two valves, one for live steam, the other to the exhaust line. The lower connects thru valves to cold water supply steam and exhaust respectively.

A pressure gauge is provided on the autoclave just to the right of the three-way connection.

As considerable power is required to operate the stirrer in the dry and moist salt the autoclave legs are anchored in concrete by bottom plate and anchor bolts. The stirrer revolves once every minute.

Purification of Crude Sodium Salt.

The source of impurities has already been covered under "Chemistry" and the removal of the worst of these is the next consideration. The amount of impurity in the crude sodium salicylate is indicated by the color. If a good white phenol and clean alkali are used and the temperature of the autoclave carefully regulated, the crude sodium salt is light brown or yellow, almost white, and requires no preliminary purification previous to freeing the acid, but if a red phenol or poor alkali are used and the temperature rises even temporarily above 145° , the product will be dark or red in color and will require purification.

The colored salts if precipitated directly from water solution by acid, separate with admixture of considerable quantities of tar. If the mixture is boiled with considerable water the acid will dissolve and may be decanted from the mass of tar which collects. On cooling, salicylic acid separates in crystals which are always more or less colored. Recrystallization and washing do not improve this and this colored acid always contains free phenol.

Attempts to remove this color by boiling and filtering with fullers earth or animal charcoal were only successful up to a certain point beyond which they seemed to have no action.

Hoffman (DRP 65131) patented a method of purifying crude sodium salicylate by means of stannous chloride. The crude salt was dissolved in a large quantity of boiling water and treated with stannous chloride solution until the upper layer of liquid was water white. This method was tried with success. The badly colored crude salt was dissolved in 30 parts of hot water, and different amounts of crystallized stannous chloride added. The solution was kept at about 90° until the solution became clear and colorless. Depending upon the amount of color to be removed, the stannous chloride required varied from 5 to 20% of the weight of the crude salt. Stannic hydroxide is precipitated in amount equivalent to the stannous chloride oxidized by the precipitation of tar. The excess stannous chloride is precipitated as stannous hydroxide by the excess of alkali present. If too large an excess of tin salt is added and there is not a large enough excess of alkali present, a fine colloidal precipitate of basic chloride is formed which is difficult to filter. This should be precipitated by adding more alkali. The precipitated tin compounds are filtered off with the tar from which they are separated by dissolving in concentrated HCl. Stannous chloride may be regenerated by reducing with metallic tin or tin may be precipitated by replacing with granulated zinc.

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Purification of Free Acid.

It should be understood that the previous purification process removes only tarry material (which is semi-volatile in superheated steam) and does not remove free phenol, meta- and para- acid, or hydroxy iso-phthalic acid. If the colorless solution of sodium salicylate is made quite acid with hydrochloric acid in the cold, free salicylic acid is precipitated in a mass of needles. These are separated from the mother liquor by filtration and well washed with cold water; this washing removes the greater part of the para- acid and phenol but the crystals may still be contaminated with iron oxidation products and hydroxy iso-phthalic acid. (NaCl removed also).

Reuter discovered that salicylic acid was volatile in steam superheated to 170° at ordinary pressures (atmospheric) (B. 2,537 /1875/). If the washed acid, then, is distilled in steam the traces of para- and meta- acid which are not volatile in steam along with the hydroxy iso-phthalic and iron compounds which are equally nonvolatile will be eliminated.

Water solutions of salicylic acid, not ones in particular, exhibit a marked solvent action upon many metals. As the condenser for the steam distilled acid necessarily had to be of metal, it was necessary to find what metals might be used. Reuter gave silver as the best and this was confirmed. Tin may also be used

but the acid on striking this metal tends to stick in hard lumps. Iron, copper, nickel and Monel metal gave colored products while zinc gave an opaque white crystal.

For some purposes the trade demands sublimed acid. This is made by heating steam distilled acid to 200° in a tin lined pot over which is placed a small tight fitting wooden keg as a condenser. This temperature must be carefully regulated as the tin lining melts at 231° and also the acid starts to decompose at 210° .

The Complete Process.

From the foregoing data the final method of operation was developed, which has since been successfully employed.

The autoclave used has been already described in detail (Fig. 4.) The finished machine ready to be installed is shown in Fig. 5, with side wall, top and bottom heavily lagged with asbestos. Connection was made to a jet condenser and high speed steam vacuum pump thru the three way connection (V. Fig. 5). On the floor above the autoclave is a steam-jacketed kettle of 150 gal. capacity with a hinged cast iron lid. A 500# drum of phenol is washed by a stream of water from a hose before opening, the bung removed and the drum placed in the kettle, opening down, with the help of a chain block and tackle. The lid of the kettle is then lowered (not air tight) and steam at 75# pressure admitted to the jacket. In the course of half an hour the phenol melts and as the drum is slowly lifted from the kettle runs out. This is allowed to cool but not solidify, and a mechanically operated stirrer (propeller) introduced. 70 gal. water are then added and 220# of 98% NaOH in portions never allowing the mixture to boil. When all dissolved, the cover is lowered, after removing the stirrer, and kept at about 90°C. until wanted.

This kettle communicates thru a valve at the

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Fig. 5.

bottom with a three inch iron pipe leading to the center three-way connection on the autoclave, a second valve being placed here. The inside of this pipe at the flange is threaded and a 3"-1" male reduction coupling screwed in. The purpose of this is to form a nozzle which directs the stream of sodium phenate solution directly onto the bottom of the autoclave and so avoids filling the side connections and passage to the pressure gauge.

When the sodium phenate solution is ready, the autoclave is heated by opening the upper jacket steam valve (and lower exhaust) and the vacuum turned on. All other valves must be tightly closed. The lower valve on the phenate line is then opened and then the valve to the mixing kettle. The pressure of the atmosphere forces the sodium phenate solution rapidly into the autoclave, when the two valves are closed. The capacity of the autoclave is over 300 gal. and the volume of solution added only 130 gal. so twice that amount may be treated if desired. Maintaining the vacuum as high as possible the stirring mechanism is started and jacket pressure kept at 75%. Heating and stirring are continued until the sodium phenate is absolutely dry. The temperature must be carefully watched so that it does not rise above 160° and under no circumstance must the stirring mechanism be allowed to stop, or the mass will set and require dismantling of the apparatus to get it out. If for any reason the power should fail, men should be used to furnish

power until water can be run in and the material gotten into solution. After the mass has set it is impossible to start the stirrer and equally impossible to get into solution without the help of crowbar and pick (as has been learned by sad experience). The time required for this drying operation is about one hour and a half. At the end of this time the jacket steam is shut off and also the bottom exhaust. The upper exhaust valve is now opened wide and both steam and cold water are admitted thru the bottom jacket connection by their respective valves. The water valve is gradually opened and the steam valve closed. The steam is used at first so as to prevent straining the autoclave by too sudden temperature changes. The vacuum and stirring are continued, the cooling water flowing until the temperature of the dry phenate has fallen to 100°. The vacuum may then be released and carbon dioxide admitted. If the gas is turned on before the 100° point is reached there will be a sudden evolution of heat and the product burned as will be shown by the bad color and subsequent yield of tar. The cooling operation requires two hours as against the twelve hours necessary for the older apparatus (Fig. 1).

This charge requires 234# of carbon dioxide which is furnished by 100# cylinders of compressed gas. The pressure desired in the autoclave is 90# per sq. in.; cylinder gas is under 200#

pressure and therefore a reducing valve is used. The main regulating valve is at the autoclave next to the safety valve which blows off at 100#. A two branch manifold, each branch having a shut-off, and connected to three gas cylinders, supplies the reducing valve. The object of using two separate sources of gas is to be able to use as much gas as possible from each cylinder. The reaction may be started and progress rapidly at first using low pressure gas, but the last two thirds requires 90# pressure if time is an object. The procedure is to connect three cylinders whose pressure has fallen below 90# to one branch and to use these when starting to carbonate until exhausted, which they do very quickly. Then the other branch with three fresh cylinders is turned on, after shutting off the low pressure branch, and the reaction finished at 90#.

During the carbonating period, the time required being one to two hours according to the skill of the operator, the rate of admitting carbon dioxide, the amount of steam or cold water to the jacket, the temperature should be as near 140° as possible but under no case should be over 145°. Complete absorption is indicated by no fall of pressure when the supply of carbon dioxide is shut off. The stirrer operates without stop during this time. The autoclave is now nearly filled with

THE UNIVERSITY OF CHICAGO

THE DIVISION OF THE PHYSICAL SCIENCES

DEPARTMENT OF CHEMISTRY

CHICAGO, ILLINOIS

RECEIVED

APRIL 10, 1954

FROM

DR. J. H. GOLDSTEIN

CHICAGO, ILLINOIS

TO

DR. J. H. GOLDSTEIN

CHICAGO, ILLINOIS

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water after first opening the exhaust valve to carry away the steam evolved. This heating, with the continued stirring, causes solution to be brought about quickly. The stirrer is now stopped for the first time in such a position that the bottom stirrer arm does not prevent opening the discharge valve; the hand wheel which locks the valve is turned down and the foot pedal depressed and locked. Steam is also admitted above the liquid to shorten time to empty. After this hot water is used to wash out the autoclave which is then thoroughly dried by heating.

The solution of crude sodium salicylate should be clear and of a straw or light brown color. Such a solution, which should be the result if phenol with a melting point not below 39.2° and which does not turn red on melting, is used and if the salt has not been burned, requires no preliminary treatment before precipitating. Badly colored solutions are run into a 350 gal. kettle, treated with stannous chlorid solution (1.827 sp.gr.) and agitated and heated by direct steam until the solution is colorless. The precipitated tar and tin is removed by filtering thru a Filtros vacuum filter, the clear liquid being run into a 400 gal. glass enameled tank. Tin on the filter is recovered and separated from the tar by dissolving in concentrated HCl, and reducing to stannous chloride by addition of metallic tin or if too badly contaminated with acid-soluble tar

may be precipitated as metallic tin by addition of granulated zinc or blue powder.

The clear purified sodium salicylate solution is now treated with 63 gal. of 20°Be: (32%) commercial HCl. If by any chance this amount of acid does not make the solution strongly acid to litmus, more must be added. Fine, white needles of free salicylic acid are precipitated in clouds. The precipitation should be carried out on the solution while hot. As the solution cools the fine crystals grow, which makes filtration more rapid as then a springy matt is formed. Filtration is accomplished in a convenient way, simply by lowering an enameled perforated pipe around which is tied a bolting silk bag to the bottom of the tank and applying suction to the other end. The crystals left in the tank are washed twice with water as cold as possible, the first washing only going with the mother liquor. The mother liquor is evaporated in an enameled kettle until crystals begin to form, cooled and the free acid treated as before. It is not necessary to thoroughly dry the salicylic acid at this stage, but it is surprising to see how dry the product is if the crystals have been allowed to grow properly.

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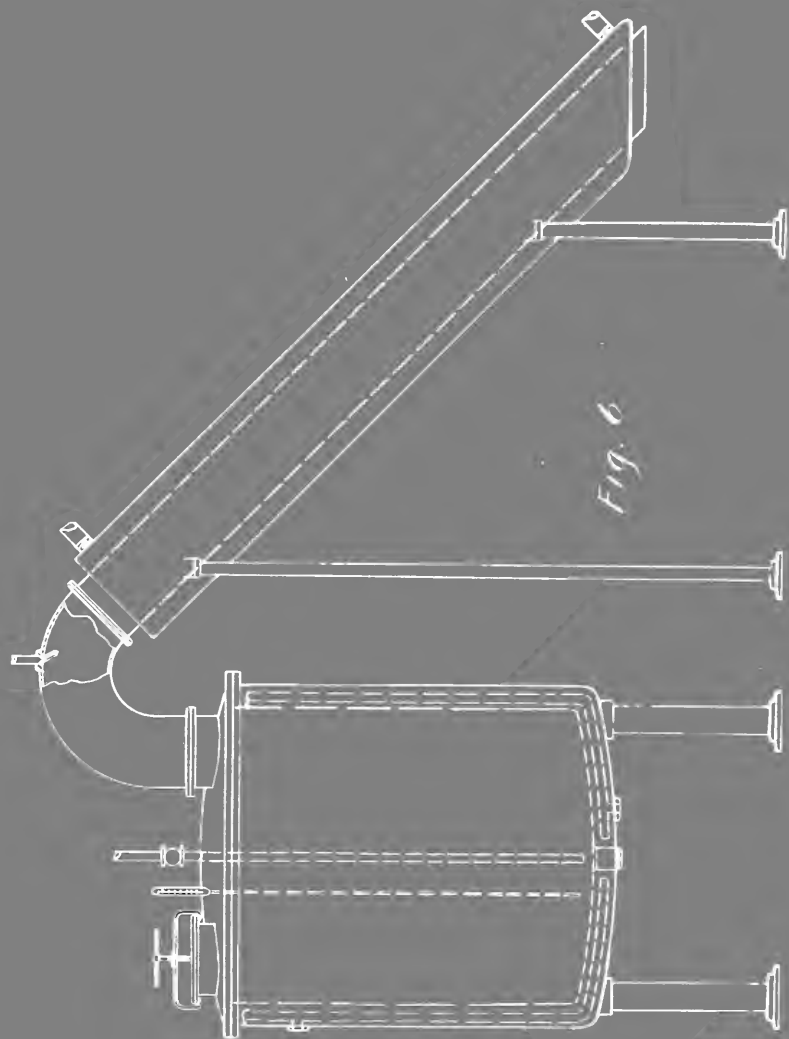
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Steam Distillation.

The final purification of salicylic acid is accomplished by distilling it in steam. To do this the acid must be melted first and then brought in contact with steam at atmospheric pressure or very slightly higher, superheated to 170°C . The temperature of the molten acid and of the superheated steam must under no consideration exceed 175° or phenol will be found in the product. Low pressure steam must be used as even slight increases in pressure raise the volatilizing point so much that the acid decomposes before it can be carried over by the steam. The regulation of the still and steam temperatures requires constant attention and the system used here was designed with the idea of making this regulation as easy as possible.

The still used is shown in Fig. 6. The kettle is 2ft.9in. in diameter and 3ft.3in. deep. It is steam jacketed and tin lined up to the first pipe flange. The superheated steam is introduced thru the pipe at the center. A thermometer is also provided as shown. The water cooled condenser has an inside diameter of 8in. and is 7ft. long. At the top of the goose neck a spray nozzle, pointing down the condenser, is placed. This is used to wash the condenser free from accumulated crystals which might stop it up in time. The first condenser tube and goose neck were lined with silver but these have been quite recently replaced with enameled steel at a much lower cost







and without changing the character of the process. All joints are protected by soft tin gaskets. As it was impossible to keep the temperature of the jacket constant simply by maintaining constant steam pressure, as operations in other parts of the plant affected this considerably, a regulator was provided on the kettle communicating with the jacket space. This regulator or warning signal as it might better be named will be described in detail later.

The superheated steam system is somewhat complicated as it is necessary to regulate the temperature within at least five degrees. Fig. 7. shows the system used: Exhaust steam enters the separator thru valve V_3 and is there rid of oil and water. The clean steam is then divided, part passing thru the superheater and the rest going directly to the mixing chamber thru valve V_2 . The superheater is of the Foster type, gas fired and works most efficiently when superheating to a temperature of 360°C . Fig. 8. shows the kind of tubes used, 12 in number, 1 inch in diameter by 34 inches long and made with drawn steel tubes and cast steel rings. The required temperature is gotten by mixing the proper proportions of saturated and superheated steam by regulating valves V_1 and V_2 . After being thoroughly mixed by baffles in the mixing chamber the steam passes by two pipes into the "regulator" and thence to the still.



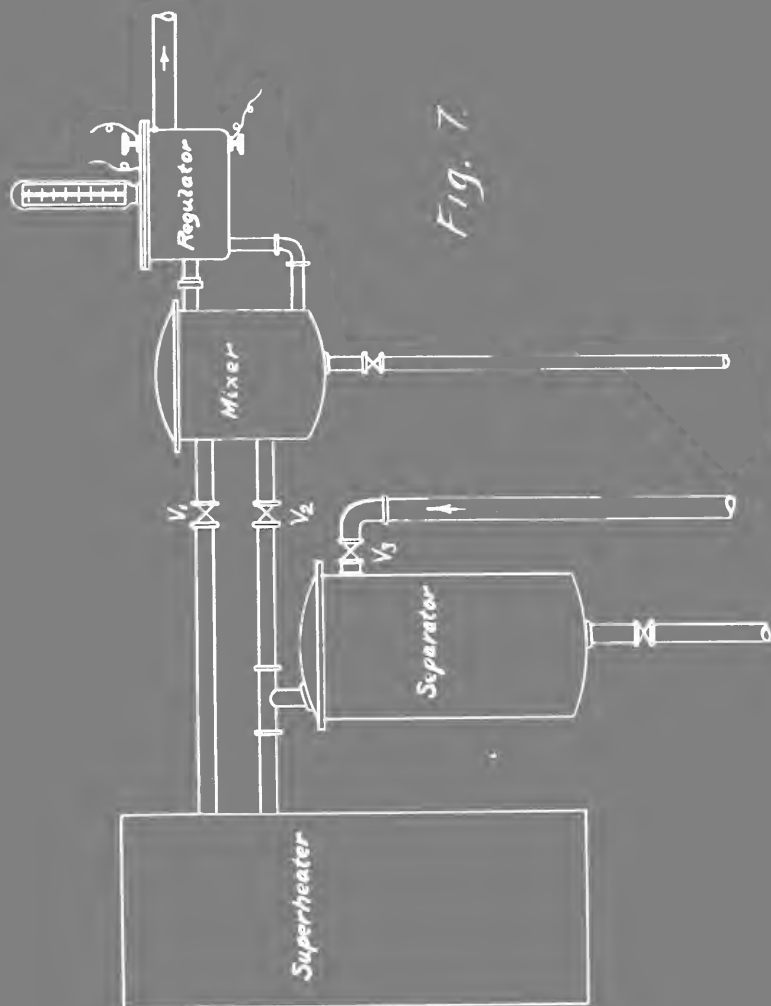
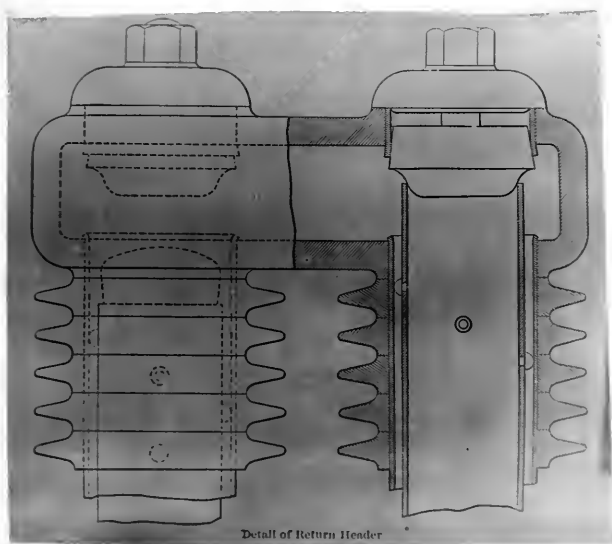


Fig. 7





Detail of Return Hender

Fig. 8.



A detailed drawing of the regulator is shown in Fig. 9. full size. The body is cast iron 5in. long by 1 1/2in. wide. Thru the cover and bottom pass two platinum tipped screws with a very fine thread. These pass thru copper bushings which are insulated from the rest of the case by Bakelite molded in place. The cover carries a half inch square stud into the end of which is screwed the regulator strip. This is made of two strips of metal, each 3/64" thick, 9/16" wide and 4 1/2" long. These are made of "Invar" and "Magnalium" respectively and are riveted tightly together, the Invar being on top. A double tipped platinum contact screw goes thru the end and held by two lock nuts. The coefficient of expansion of Invar is practically zero, while Magnalium has a high one. Hence when the riveted combination is heated, the Magnalium expands, while the Invar does not, the result being that the end of the strip is bent upward causing the upper tips to make contact. When cooled the reverse action takes place, the two lower tips making contact. The adjustable screws are so set that when the thermometer reads 171° the regulator contacts are equidistant from the two regulating screws. In addition the upper screw is set so that it makes contact at 173° and the lower screw set to contact at 168°. The connections first used were the alarm system (Fig. 10) The regulator points on the still jacket are to the right, those on the steam line to the left. The current used is supplied by a small transformer or direct current



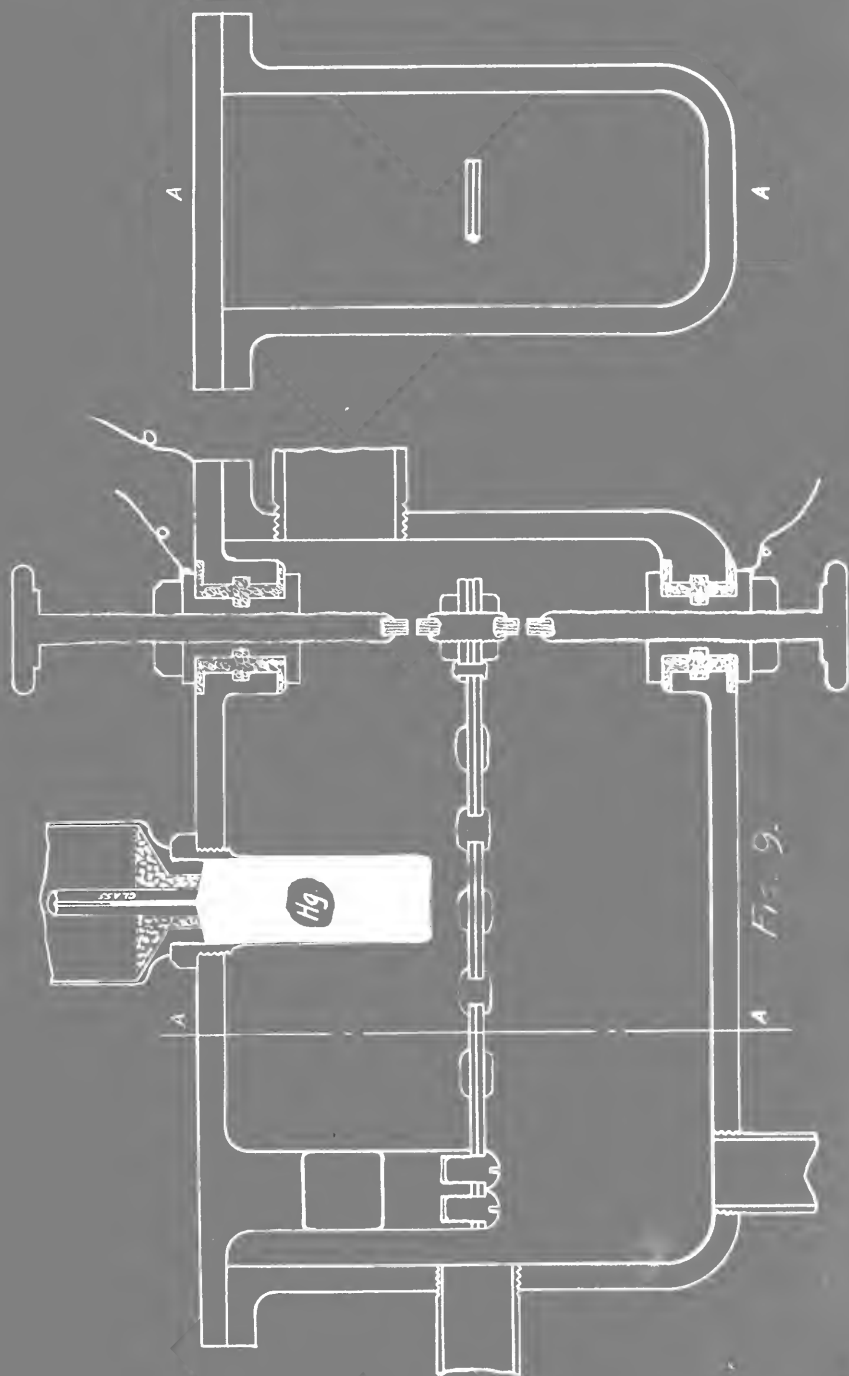
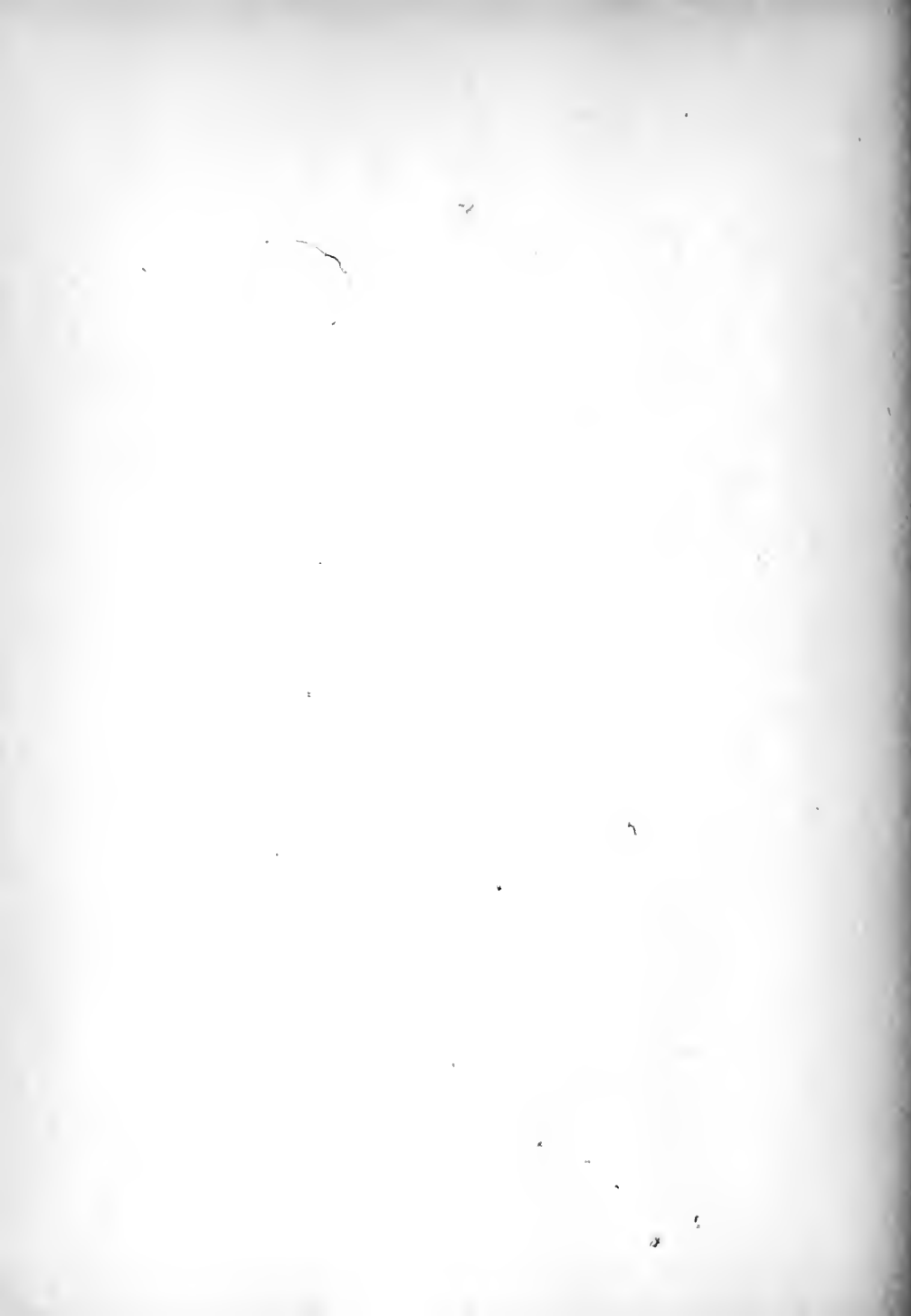


Fig. 9.



at 6 volts. The double circles represent lamp. 6volt miniature electric lamps in circuit with the electric bell. Say for instance that the temperature of the kettle reaches 173° . The upper contacts close completing the circuit and thus causes the bell to ring and light 3 to glow. If the temperature is lowered to the correct point (below 173°) by the operator the circuit is broken and the bell stops ringing and the lamp goes out. If, say, the temp. of the superheated steam drops below 168° the lower contacts on that regulator close causing the bell to ring and lamp 2 to light. If two contacts close at the same time the bell rings and two lamps light. The temperature of the superheated steam is raised by opening valve V_1 or closing V_2 (Fig. 7) or both and vice versa.

More recently an automatic control has replaced the signal system on the superheat line, the signal system being retained on the kettle which does not require such constant regulation. Fig. 11 shows these connections: The regulator contacts now operate a 110volt relay which in turn operates two solenoids one of which opens valve V_2 (Fig. 7), the other closing it partially. If the temp. rises too high, the upper contacts close as before closing the relay to the right and thus admitting 110 volts to the solenoid



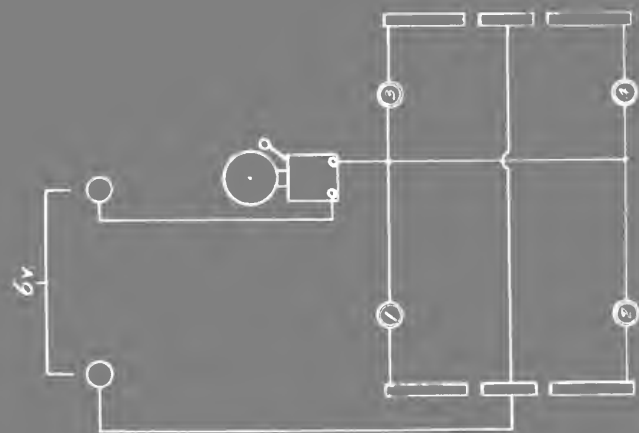


Fig. 10.

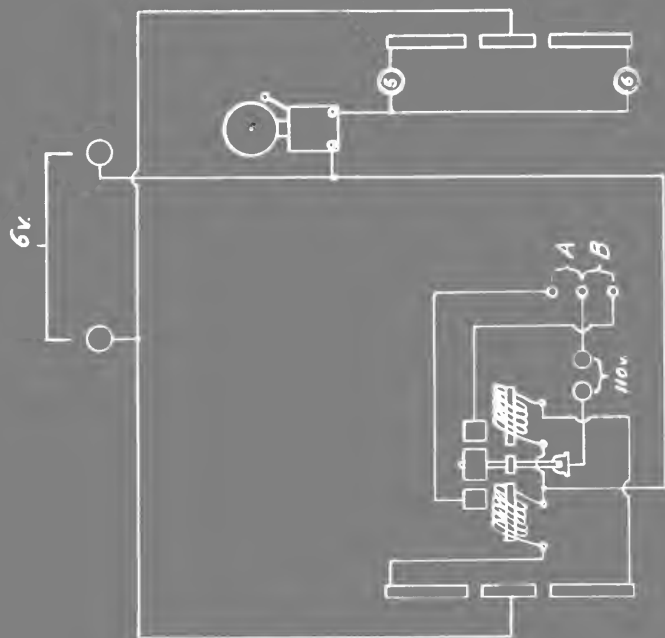


Fig. 11.



connected across A, which opens valve V_2 thus admitting cold steam to the mixer. The solenoid which returns the valve to its original position is connected across B and is operated by the lower contact points. This method maintains the superheated steam temperature at $170 \pm 2^\circ\text{C}$. The same system might be applied to the kettle valve but much larger solenoids would be required because of that valve carrying steam under considerable pressure.

The crystal size may be regulated easily by the volume of steam admitted and by the amount of spray used in the condenser. Large volumes of steam and small amount of spray give large crystals which are desirable.

The mixture of distilled acid and water is collected in large enameled buckets which are cooled in water and then dumped into a 30" centrifuge with tinned basket and enameled shell. The crystals are completely dried after whirling by spreading in enameled pans 3ft. square by 3 1/2" deep and placing in a vacuum oven for one hour at 100° . The dry product is packed in 1# and 5# double paper bags. The centrifuge liquor is used to make up fresh sodium phenate solution. The yield of pure acid from a good crude is about 95%. A tarry crude may give as low as 80%. 100% yield on 500# phenol is 734#. Fig. 12 shows the vacuum oven used and Fig. 13 a distilling plant for benzoic and salicylic acids erected at Leipzig by "Opitz u. Klotz" handling 10,000# acid per day.



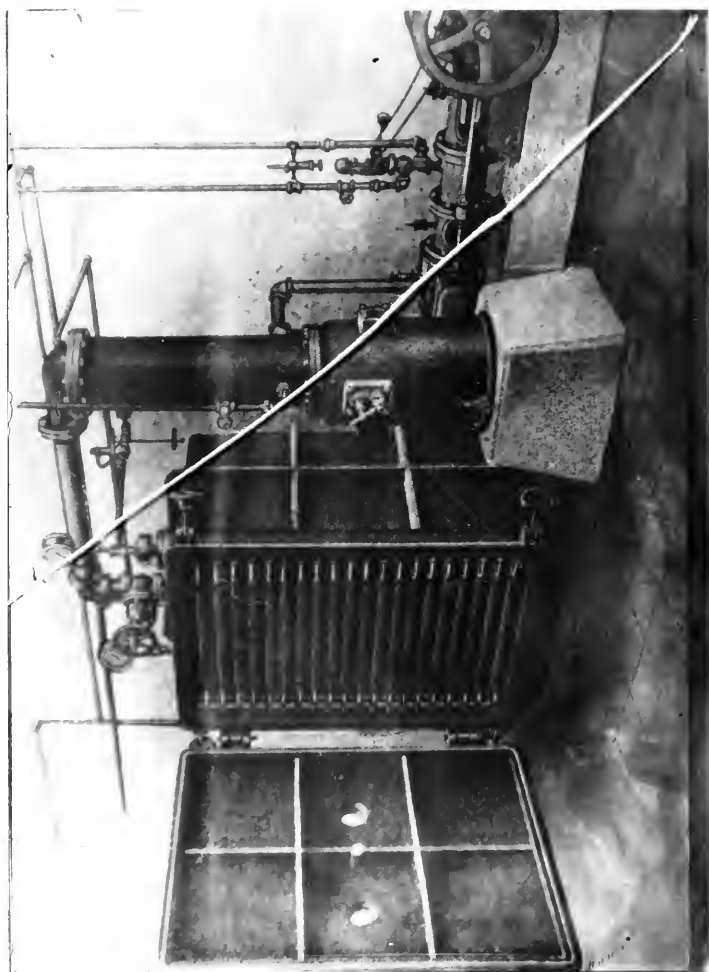
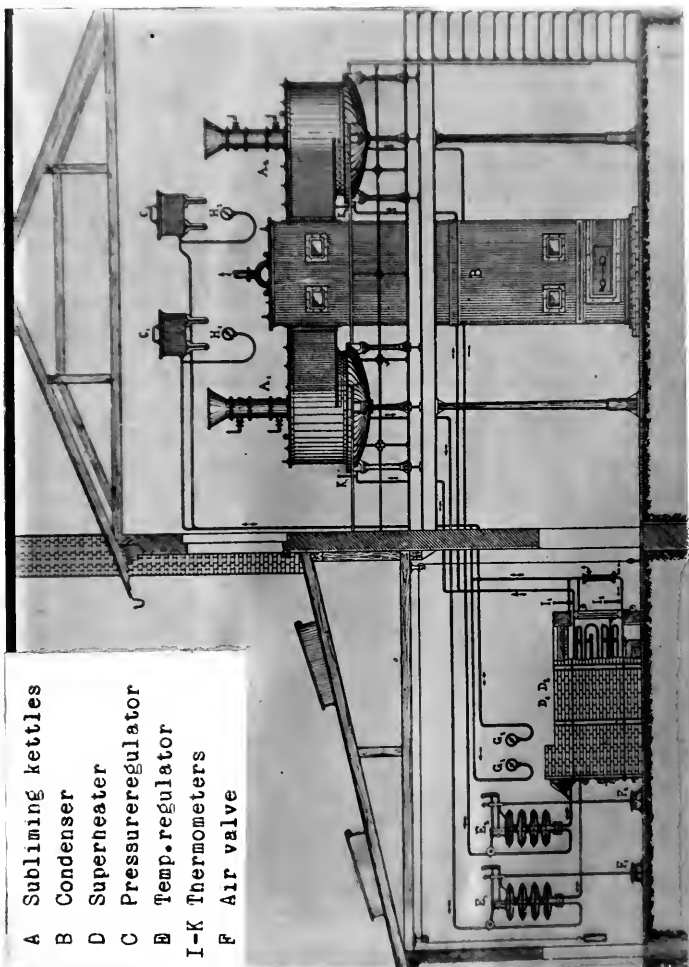


Fig. 12.





- A Subliming kettles
- B Condenser
- D Superheater
- C Pressureregulator
- E Temp. regulator
- I-K Thermometers
- F Air valve

Fig. 13



Manufacture of Sodium Salicylate.

As sodium salicylate is demanded as much if not more than the acid and as its manufacture requires special apparatus and technique, it is thought best to include it here.

Sodium salicylate is made from the wet acid from the centrifugal machine. It is first necessary to determine its moisture content. This is done by drying about 10 gm. in vacuum at 80°. Centrifuged acid contains as a rule about 4% moisture. 165% of dry acid equivalent is placed in the enameled dehydrating pan (Fig. 14) which rests in a shallow tank of water kept at 60°C. 5 gal. distilled water are added and the mixture stirred. 100% of the highest quality sodium bicarbonate are now added and well stirred, carbon dioxide being evolved. When the evolution of gas ceases the pan is closed and connected to vacuum and the temperature raised to 60°, not more. The heat, vacuum and stirring are continued until the salt is absolutely dry, which takes about six hours. This forms the granulated salt which may be removed and immediately bottled.

An excess of acid is used because the salt if alkaline in reaction turns brown as it also does if left in contact with air or dried above 60°. Sodium salicylate crystallized from alcohol is also demanded. To the dry salicylate in the pan is added 50 gal. 96% ethyl alcohol and heated to 75° with stirring until dissolved. The

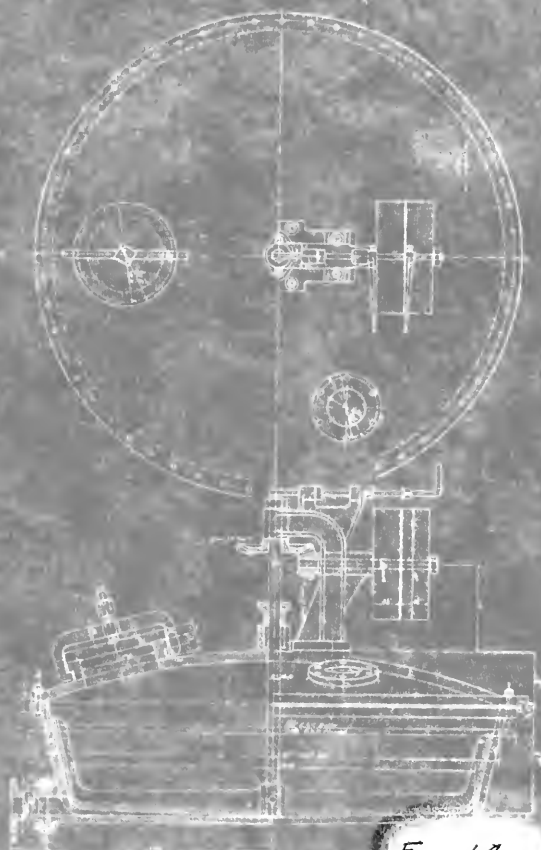


Fig 14



solution is then run while hot, quickly into the enameled trays before mentioned (page 33). After standing a few moments the solution solidifies into a stiff jelly-like mass. The trays are placed in the vacuum shelf drier at 80° and the alcohol which distills is caught in the surface condenser; 97% recovery of alcohol. One half hour of this treatment thoroughly dries the salt which may then be removed and bottled. Yield 100% or 191%. The alcohol used should contain about 1% ether which prevents darkening.

When it is necessary to make up sodium salicylate from dry acid, the acid is placed in an enameled box and about five percent distilled water added. This is worked into the acid to wet it by a man with a tinned paddle. If it were attempted to add bicarbonate and water to the dry acid, the acid would float almost indefinitely and not react.

It may also be noted here that the sodium salicylate used in the manufacture of salol is not the pure product but the crude salt obtained from the autoclave.

Notes.

During the course of this work it was necessary to know various facts concerning solubility, means of separating mixtures of these allied bodies, and methods of analysis, all of which may be found possibly in the literature but widely scattered. It has, therefore, been thought advisable to include these facts, the reference in each case being that one which most nearly agreed with these results:

Solubility-

Grams salicylic acid per 1000 cc water. (Seidell)

t°C.

0 ---- 0.8	30 ---- 2.7	70 ---- 13.2
10 ---- 1.2	40 ---- 3.7	80 ---- 20.5
20 ---- 1.8	50 ---- 5.4	100 ---- 76.9
25 ---- 2.2	60 ---- 8.2	(1 gm per 13 cc)

per 1000 cc ethyl alcohol.

t°C.

-32 ---- 36.12	+15 ---- 49.63	21 ---- 52.53
	15-90% - 42.09	

per 900 gm benzol.

t°C.

11.7 ---- 0.46	30.5 ---- 0.99	49.4 ---- 2.38
18.2 ---- 0.58	34.6 ---- 1.26	64.2 ---- 4.4

Sodium salicylate is soluble in an equal weight of cold water, slightly soluble in absolute alcohol, and in 8 parts of cold spirit.

(Allen)

	Salicylic acid	para-acid
water at 0°	1 pt in 1100	1 in 580
water at 15°	1 pt in 1000	1 in 126.
chloroform	readily	slightly.

Meta and para-acid and hydroxy iso-phthalic acid are not volatile in steam.

A mixture of salol, salicylic acid, and phenol may be separated by dissolving the salicylic acid in sodium bicarbonate solution, then removing the phenol by dissolving in sodium hydroxide and leaving the salol behind.

Purified (?) salicylic acid may contain hydroxy iso-phthalic acid if not steam distilled and may be detected by distilling in steam when the impurity is left behind (with m- and p- acid) as a grey powder.

Phenol may be present in sublimed acid. 0.02% may be detected by dissolving 0.25gm in 5cc cold water in test tube and adding two drops of 2% sol. of fuffuraldehyde in alcohol and shaking gently. Pour 2-3cc concentrated sulphuric acid carefully to the bottom. A yellow ring forms at junction, a blue ring appearing above with rapidity depending upon amount of phenol present.

Para-cresotic acid may be determined on dry acid by titrating with N/20 baryta with phenolphthalein. 1gm pure acid reqs. 724.4cc. 1% cresotic acid lowers vol. reqd. by 0.688 cc.

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The following table shows the number of persons who have been admitted to the office of the Secretary of the Board of Education, from the year 1870 to 1899. The number of persons who have been admitted to the office of the Secretary of the Board of Education, from the year 1870 to 1899, is as follows:

Year	Number of persons admitted
1870	1
1871	1
1872	1
1873	1
1874	1
1875	1
1876	1
1877	1
1878	1
1879	1
1880	1
1881	1
1882	1
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1890	1
1891	1
1892	1
1893	1
1894	1
1895	1
1896	1
1897	1
1898	1
1899	1

Key to Sample Plate.

1. Crude sodium salicylate (purple).
2. No.1 precipitated by HCl.
3. No.1 precipitated by HCl after treatment with fullers earth.
4. No.1 precipitated by HCl after treatment with animal charcoal.
5. No.1 precipitated by HCl after treatment with stannous chloride.
6. No.2 distilled with steam.
7. No.5 distilled with steam.

8. Crude sodium salicylate (brown).
9. No.8 precipitated by HCl.
10. No.9 distilled with steam.
11. Small steam crystals.
12. Normal steam crystals.
13. Large steam crystals.
14. Very large steam crystals (slightly contaminated with iron).
15. Crude sodium salicylate (yellow).
16. No.15 precipitated by HCl.
17. No.16 steam distilled.
18. Salicylic acid crystallized from alcohol.
19. Sublimed salicylic acid.
20. Acid from Monel metal condenser.
21. Milky acid from zinc condenser.

22. Acid from iron condenser.
23. Acid from nickel condenser.
24. Acid from copper condenser.
25. Pure lump sodium salicylate made at 60°C.
26. Pure lump sodium salicylate made at 100°C.
27. No.25 crystallized from alconol.
28. No.26 crystallized from alconol.

